Thermal Dissociation of Excitons Bounds to Neutral Acceptors in High-Purity GaAs†

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The dissociation of excitons bound to neutral acceptors in GaAs is investigated by measurements of the temperature dependence of the integrated emission. Two dissociation processes are observed for all acceptors. Dissociation of holes reduces the emission starting at about 6 K, while from about 10 K upwards a dissociation of both holes and electrons dominates. The binding energies of the holes and of the electrons bound to the neutral acceptors are evaluated. The spectral positions of ionized acceptor-exciton recombination lines are predicted and verified. A formula is derived which describes the measurements quantitatively.

I. INTRODUCTION

The near-gap luminescence of high-purity GaAs at low temperatures is dominated by the recombination of bound excitons.[1–4] There are only very few measurements of the temperature dependence of the luminescence of GaAs[2] and other III-V compounds.[5] Excitons bound to neutral acceptors have not yet been studied. In GaAs the acceptor Sn[3] and the effective-mass acceptors[4,6] are known to bind excitons. This paper is concerned with the temperature dependence of the integrated luminescence intensity resulting from excitons bound to different acceptors. We interpret the data with a simple model and deduce the details of the dissociation processes from the data. The binding energies of the electron and holes to the neutral acceptor are evaluated, and the spectral positions of the excitons bound to the ionized acceptors are predicted and verified.

II. EXPERIMENTAL

The GaAs crystals investigated have been grown by liquid phase epitaxy at the Fernmeldetechnisches Zentralamt der Deutschen Bundespost (FTZ) at Darmstadt, Germany, as well as at Varian, Palo Alto, California, U.S.A. Table I shows the electrical properties of some of the crystals used in our experiments. The luminescence measurements between 5 and 20 K were performed with a variable-temperature exchange-gas cryostat and a 1-m Czerny Turner spectrometer. The luminescence was excited by the green 514-nm line of an argon ion laser. Additional measurements between 4.2 and 1.5 K were made with an immersion cryostat. The emission intensity is nearly temperature independent in this temperature region; we therefore omit these data.

TABLE I. Electrical data of GaAs samples.

		293 K		77 K	
Sample	Dopant	$n_D - n_A$ (cm^{-3})	μ ($cm^2/V\,sec$)	$n_D - n_A$ (cm^{-3})	μ ($cm^2/V\,sec$)
VE 2	Sn	7×10^{14}	···	7×10^{14}	···
F 292	···	···	···	1.8×10^{13}	148 000
F 2084	···	2.4×10^{13}	7750	2.5×10^{13}	107 480

III. RESULTS

Figure 1 shows the near-gap luminescence of the samples of Table I. The lines which result from the radiative recombination of neutral acceptor-exciton complexes are marked with *A*, *B*, and *C*, respectively. The Sn acceptor is the binding center in case *A*.[3] The triplet *B*, *B′*, *B″* in Fig. 1(b) as well as the doublet *C*, *C′* in Fig. 1(c) show replicas which correspond to two-hole transitions.[4,6] The binding centers are effective-mass acceptors in cases 1(b) and 1(c). This is deduced from the spectral positions $\hbar\omega^+$ of the lines and of the binding energies E_B of the excitons, respectively.

Figure 2 shows the integrated intensity of the two lines *A* and *C* vs $1/T$ in a semilogarithmic plot. The intensity always saturates with decreasing temperature. Above 10 K the intensity decreases exponentially with an activation energy E_{T_2}. Exact evaluation shows that two activation energies E_{T_1} and E_{T_2} are necessary for a satisfactory fit of Fig. 2. Table II shows these two energies obtained from the fitting procedure in columns 5 and 6. Column 3 shows the energy difference $\Delta E = E_g - \hbar\omega^+$. E_g is the energy of the band gap in GaAs.[7] $\hbar\omega^+$ results from the energetic position of the bound-exciton recombination line. ΔE is the sum of the energy E_X of the free exciton and the binding energy E_B of the free exciton to the attractive center:

$$\Delta E = E_g - \hbar\omega^+ = E_X + E_B . \quad (1)$$

The fourth column lists the computed binding energy E_B, where Eq. (1) and $E_X = 4.9$ meV[6] is used. It is

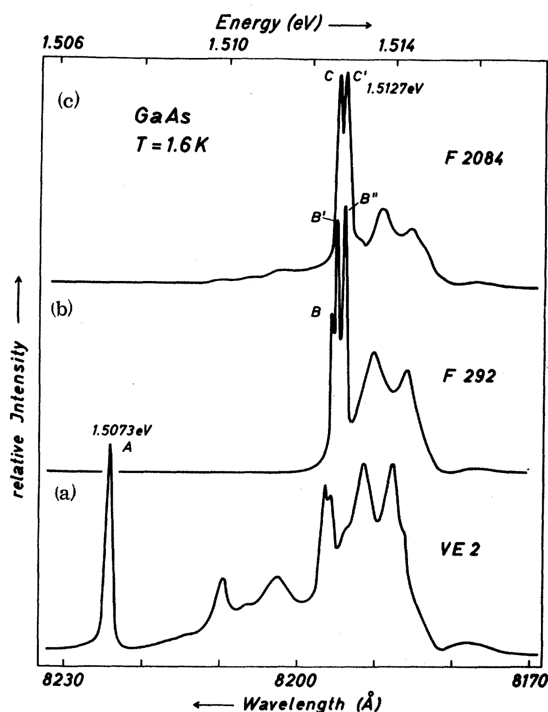


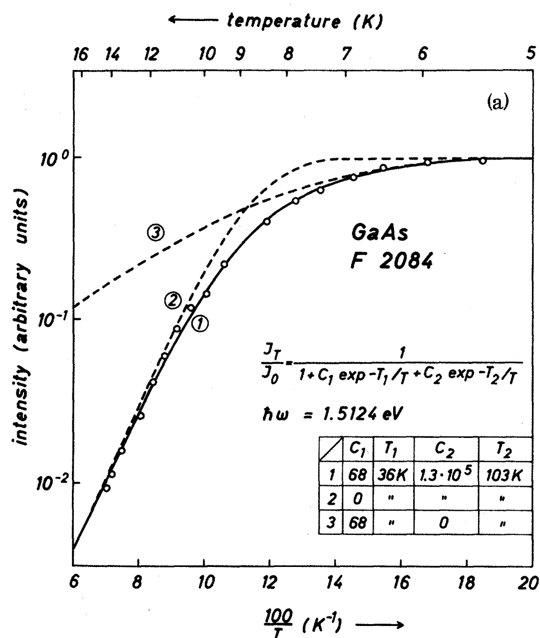
FIG. 1. Near-gap luminescence of the samples of Table I. The lines which were investigated are marked with A, B, and C, respectively. One of the lines of the triplet B is assumed to be caused by internal strain.

assumed that E_g is temperature independent in the region of interest.[8]

IV. THEORY AND DISCUSSION

The experimental results cannot be fitted with one activation energy only. This is evident from a comparison of the measured points and the dashed lines in Fig. 2. The dashed lines represent best fits of the lower- and higher-temperature parts of the measurement where a formula proposed earlier by Williams and Eyring[9] has been used, based on only one activation process. Some authors[2,5] made attempts to describe the behavior of excitons bound to donors in GaAs and GaP with this formula. Attempts to fit our data with this formula failed. We therefore have to assume that our exciton complex has a ground-state energy E_0 and at least two channels of dissociation with energies $E_{T_1} = E_1 - E_0$ and $E_{T_2} = E_2 - E_0$. Stated in another way, we assume that the bound-electron-hole pair constituting the exciton complex has at least three states: a ground state of energy E_0, where it is bound, and two higher states of energies E_1 and E_2, where it is dissociated.

We now calculated the average number $N_0(T)$ of bound-electron-hole pairs which are in the bound ground state E_0 at a fixed temperature T. We start from the following assumptions: (i) Each electron-hole pair may be thought of as a complete system, the rest of the crystal including all the other electron-hole pairs merely serving as a temperature bath. This assumption means that pair-pair correlations are negligible. (ii) The three-level system is in thermal equilibrium with the crystal of tem-



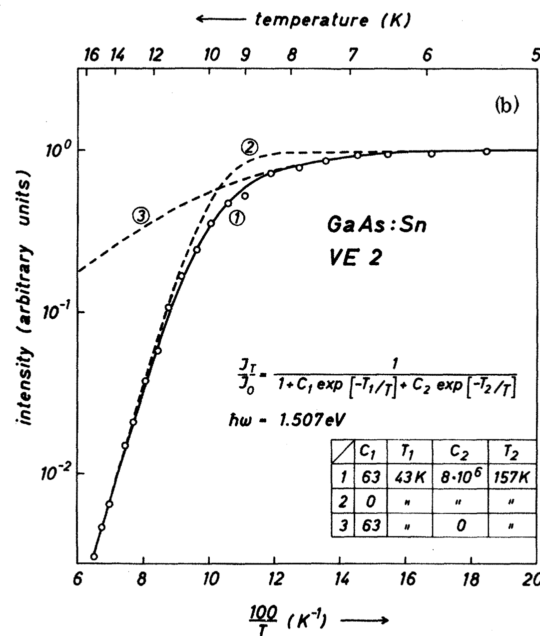


FIG. 2. Integrated intensity of (a) the line A and (b) the lines C and C' in a semilogarithmic plot. The open circles are experimental points. The dashed and straight lines are theoretical fits with either one (dashed) or two (straight) different dissociation energies derived from Eq. (7).

TABLE II. Luminescence energy $\hbar\omega^*$, calculated binding energy E_B of the exciton to the neutral acceptor, and activation energies E_{T_1} and E_{T_2} from the fit to the temperature-dependent intensity in three GaAs samples.

Sample	$\hbar\omega^*$ (eV)	$E_g - \hbar\omega^*$ (meV)	E_B (meV)	E_{T_1} (meV)	E_{T_2} (meV)
VE 2	1.5070	13.4	8.5	3.7 ± 0.5	13.5 ± 1.5
F 292	1.5124	8.0	3.1	3.1 ± 0.5	9.2 ± 1.5
F 2084	1.5124	8.0	3.1	3.1 ± 0.5	8.8 ± 1.5

perature T.

With these assumptions the distribution of electron-hole pairs among the three levels is governed by the Boltzmann law, which gives

$$N_0(T) + N_1(T) + N_2(T) = N_G(T)\,, \qquad (2)$$

$$N_1(T)/N_0(T) = (\alpha_1/\alpha_0)\; e^{-(E_1-E_0)/kT}, \qquad (3)$$

$$N_2(T)/N_0(T) = (\alpha_2/\alpha_0)\; e^{-(E_2-E_0)/kT}. \qquad (4)$$

$N_0(T)$, $N_1(T)$, and $N_2(T)$ are the average numbers of bound excitons being in the levels E_0, E_1, and E_2, respectively; α_0, α_1, and α_2 are the degeneracies of these levels. $N_G(T)$ is the total number of pairs within the three levels.

Combination of the above equations leads to a formula for $N_0(T)$:

$$N_G(T) = N_0(T)\,[1 + (\alpha_1/\alpha_0)\; e^{-(E_1-E_0)/kT} + (\alpha_2/\alpha_0)\, e^{-(E_2-E_0)/kT}]. \qquad (5)$$

The temperature dependence of $N_G(T)$ is not known. We take it to be constant in the temperature range of interest. That means $N_G(T) = N_G(0) = N_0(0)$ in our case. This assumption is consistent with the experiments as seen from the good fit of theory and experiment (see below). Therefore we get

$$N_0(T)/N_G(0) = (1 + C_1\, e^{-E_{T_1}/kT} + C_2\, e^{-E_{T_2}/kT})^{-1}\,, \qquad (6)$$

where

$$C_1 = \alpha_1/\alpha_0,\;\; C_2 = \alpha_2/\alpha_0,\;\; E_{T_1} = E_1 - E_0,\;\; E_{T_2} = E_2 - E_0.$$

It is exactly this fraction, $N_0(T)/N_G(0)$, which is still available for the radiative recombination process with energy $\hbar\omega^*$, if we neglect any change in the radiative transition probability. From Eq. (6) we get

$$I_T/I_0 = (1 + C_1\, e^{-E_{T_1}/kT} + C_2\, e^{-E_{T_2}/kT})^{-1}\,. \qquad (7)$$

Equation (7) describes the temperature dependence of the neutral acceptor-exciton complexes very well, as is shown by Fig. 2. The solid line there represents the best fit of the data (open circles). The parameters E_{T_1} and E_{T_2} which were used for the fit are listed in Table II.

We shall now identify the dissociation processes leading to the activation energies E_{T_1} and E_{T_2}. There are four different processes for the dissociation of the (A^0, X) system. From these processes result different dissociation energies $E_{T_{a,b,c,d}}$ which will be compared with the measured energies E_{T_1} and E_{T_2}.

(a) Dissociation resulting in a free exciton:

$$(A^0, X) \to A^0 + X, \qquad E_{T_a} = E(A^0, X) = E_B\,. \qquad (8)$$

(b) Dissociation resulting in one free electron and one free hole:

$$(A^0, X) \to A^0 + e + h\,, \qquad E_{T_b} = E_B + E_X. \qquad (9)$$

(c) Dissociation resulting in one free hole:

$$(A^0, X) \to (A^-, X) + h\,,$$
$$E_{T_c} = E_B + E_X - E(A^0, e) = E_{T_b} - E(A^0, e) < E_{T_b}. \qquad (10)$$

(d) Dissociation resulting in two free holes and one free electron:

$$(A^0, X) \to A^- + h + h + e\,, \qquad E_{T_d} = E_{T_b} + E_A >> E_{T_b}\,. \qquad (11)$$

Beginning at about 6 K in all cases, a first dissociation process dominates with the very low activation energy E_{T_1}. In the case of the Sn acceptor (sample *VE* 2) this energy is essentially lower than the binding energy E_B of the exciton on the center as is shown by a comparison of these energies which are listed in Table II. It is obvious that only the dissociation of a free hole from the complex can cause this first intensity drop. An exciton bound to an ionized acceptor remains as described by process (c). The activation energies of the other processes (a), (b), and (d) are much too high to explain the experiments. This means that the binding energy of the second hole in the (Sn^0, X) complex is lower than the ionization energy E_X of the free exciton. Thus the neutral center is repulsive to a second hole, and a binding must be mediated by the electron. The binding energy E_e of the electron to the neutral acceptor now results from the energy balance

$$E_B + E_X = E_{h_2} + E_e. \qquad (12)$$

With this energy E_e and the ionization energy E_A of the neutral acceptor we can predict theoretically the spectral position $\hbar\omega_i$ of an emission resulting from the radiative recombination of an exciton bound to an *ionized* acceptor, because

$$\hbar\omega_i = E_g - E(A^-, X) = E_g - E_A - E_e\,. \qquad (13)$$

The binding energies of the different holes and the electron and the spectral position of the predicted (A^-, X) emission are listed in Table III. The values of $E_B + E_X$ from Table II are used to evaluate E_e.

We have now identified the process which led to the first drop in intensity in the case of the (Sn^0, X) complex as the liberation of one free hole and evaluated the binding energies of the different particles to the center. To analyze which process is responsi-

TABLE III. Binding energies of the holes $E_{h1,2}$ and the electron E_e in the (A^0, X) complex, predicted spectral position $\hbar\omega_i$ of the recombination of the (A^-, X) complex, and relative binding energy $E_e/(E_B+E_X)$ of the electron.

	$E_A = E_{h_1}$ (meV)	E_{h_2} (meV)	E_e (meV)	$\hbar\omega_i(A^-, X)$ (eV)	$E_e/(E_B+E_X)$ (%)
VE 2	171 ± 0.5[a]	3.7 ± 0.5	9.7 ± 0.5	1.3395 ± 0.001	72
F 2084, *F* 292	27 ± 0.5[b]	3.1 ± 0.5	4.9 ± 0.5	1.4883 ± 0.001	60

[a]Reference 3.

[b]J. A. Rossi, C. M. Wolfe, and J. O. Dimmock, Phys. Rev. Letters 25, 1614 (1970).

ble for the first activation in the case of the exciton bound to the effective-mass acceptors (sample F 292 and *F* 2084) is not as simple as in the case of the Sn acceptor. The measured activation energy E_{T_1} here coincides also with the binding energy E_B of the exciton on the acceptor (see Table II). Thus the activation could also take place in the form of the dissociation of a free exciton. A definite conclusion cannot be reached. Nevertheless we prefer here also process (c), dissociation of a free hole. If the hole had a much lower binding energy than 3.1 meV, we should find at lower temperatures the beginning of of a decrease of the intensity with exactly this lower activation energy. This does not coincide with our experiments. On the other hand, E_{h_2} cannot be much larger than E_B, because it cannot be more tightly bound to the acceptor than the electron. This shows a comparison with the H^- model. An independent argument for our choice of model (c) arises from the fact that we can predict on this basis the spectral position of the luminescence band of the exciton bound to the ionized acceptor. An exact investigation of our samples showed that at high excitation intensities in the predicted position indeed arises a very narrow luminescence line. This line was identified by means of Zeeman measurements as a bound exciton. Detailed information about this line will be published later.[6]

Summarizing, we can establish that increasing temperatures diminish the luminescence intensity by liberation of holes from the bound-exciton complex. The binding energy E_{h_2} of the second hole does not increase proportionally with the binding energy E_B of the exciton. This means that the relative binding energy $E_e/(E_B+E_X)$ of the electron to the acceptor increases with the ionization energy E_A of the acceptor.

Another dissociation process begins to dominate at about 9 K having the activation energy E_{T_2}. We see that the energies E_{T_2} and E_B+E_X which are listed in Table II are equal to each other within experimental error. Thus we can describe the activation process, which dominates at higher temperatures, by the dissociation of one free electron and one free hole [process (b)]. All other possible processes cannot be brought into agreement with the experiments. This identification could be confirmed by an independent measurement of the temperature dependence of the photoconductivity.

V. SUMMARY

The dissociation of neutral acceptor-exciton complexes in GaAs is investigated by measurements of the temperature dependence of the integrated emission. All investigated samples show qualitatively the same behavior. This behavior is described very well by a simple formula derived by means of Boltzmann statistics. The formula is based on the model of a two-step dissociation mechanism. At temperatures below about 6 K the intensity of the emission remains constant. At increasing temperatures free holes are liberated from the bound-exciton complexes, and the intensity of the radiative recombination decreases. The binding energies of these holes and the electrons bound to the neutral acceptors result from the measurements. The spectral position of the recombination radiation of (A^-, X) complexes is predicted. At further increased temperatures the intensity decreases more rapidly and the dominating activation process consists of the liberation of free-electron-hole pairs.

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High-Frequency Damping in a Degenerate Electron Gas*

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A closed form has been derived for the dissipative part of the complex frequency- and wave-number-dependent dielectric constant of a degenerate electron gas, $\epsilon(\vec{k}, \omega)$, valid in the limit $\omega \gg E_0$, $k < k_0$, where E_0 is the Fermi energy and k_0 the Fermi wave number. For $\omega > 2E_0$ this expression gives values of $\text{Im}\,\epsilon(\vec{k}, \omega)$ which are in excellent agreement with the results of more detailed calculations in which the difficult integrals over phase space were performed by a Monte Carlo method. The formula also appears to give good numerical estimates of $\text{Im}\,\epsilon(\vec{k}, \omega)$ for smaller values of ω (but $\omega > kk_0/m$), though its accuracy is not assured in that region. For example, in aluminum at the plasmon frequency, the asymptotic form agrees with the calculations of DuBois and Kivelson. The high-frequency formula derived may, therefore, be used to circumvent difficult numerical work in estimating the importance of electron correlation effects at high frequencies.

I. INTRODUCTION

If the random-phase approximation (RPA) is used to study the properties of a degenerate electron gas at zero temperature,[1] then one finds that the imaginary part of the frequency- and wave-number-dependent dielectric constant vanishes for frequencies above a certain cutoff:

$$\epsilon_2^{\text{RPA}}(\vec{k}, \omega) = 0 \quad \text{for } \omega \geq kv_0(1 + k/2k_0). \tag{1}$$

Here v_0 and k_0 are the Fermi velocity and wave number, respectively. The contributions to $\epsilon_2(\vec{k}, \omega)$ at higher frequencies come from multiple-particle excitations in which there are at least two particles simultaneously excited out of the Fermi sea and sharing energy $\hbar\omega$. Several investigations of such multiple-particle terms have been reported,[2-4] culminating in Ref. 4 (referred to henceforth as DK), in which DuBois and Kivelson include contributions from diagrams in which dissipation is due to the production of two particle-hole pairs. DK account for dynamic screening in the interaction between the electrons, and find that earlier calculations are incomplete in that they include dynamic screening, but overlook certain "triangle graphs" which enter to the same order. DK's results are summarized in Eq. (3.18) of Ref. 4 as a two-dimensional integral over a complicated integrand. The only numerical results that they report are for the damping at the plasmon frequency over a range of electron density.

In the present paper we have used a simpler model for the damping and have derived a closed form for the imaginary part of the dielectric constant valid for frequencies much greater than the Fermi energy E_0. By comparison with detailed Monte Carlo calculations it is found that the asymptotic expression gives excellent agreement for $\omega > 2E_0$ and provides an order-of-magnitude estimate for smaller values of ω even fairly close to the RPA cutoff, Eq. (1).

II. FORMALISM

The calculation of the dielectric constant is carried out using the notation and formalism of Ref. 5, which is briefly reviewed here for completeness.

The fundamental equation for calculation of the longitudinal dielectric constant $\epsilon(\vec{k}, \omega)$ is